

PATENT SPECIFICATION

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(54) PROCESS FOR DYEING SHEETS OR SHEET-LIKE STRUCTURES

(71) We, BAYER AKTIENGESSELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The subject of the invention is a process for dyeing and printing textile sheets or sheet-like structures which consist wholly or partly of fibres containing OH or NH groups with disperse dyestuffs by the principle of heat transfer printing or by the thermofixing dyeing method.

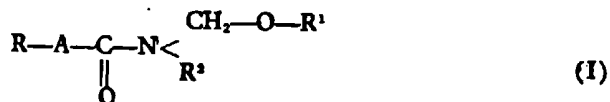
The process is characterised in that the sheets or sheet-like structure is treated with a liquor containing a) a reactive compound (as hereinafter defined) and b) a compound which catalyses this condensation reaction selected from aluminium chloride, aluminium sulphate, ammonium sulphate and zinc or magnesium chloride, nitrate and perchlorate, as well as, optionally, a fibre-swelling agent and, optionally, a cross-linking agent in order to improve the crease characteristics and after drying the sheet or sheet-like structure, the reactive compounds are fixed before employing the said printing or dyeing processes.

The term "reactive compound" (of a)) as used herein means a substance which contains, on the one hand, at least one hydrophobic hydrocarbon radical and, on the other hand, at least one reactive group which enters into a chemical bond with the OH or NH groups of the fibre material in the presence of the catalyst b) by means of a condensation reaction, that is to say elimination of, for example, water, an alcohol or a halogenated hydrocarbon. These compounds are preferably monofunctional.

Suitable hydrocarbon radicals are those with 6 to 22 C atoms. The radicals can be saturated or unsaturated, straight-chain, branched or cyclic and can be interrupted by hetero-atoms (for example O or S) and substituted by substituents (for example C₁—C₄-alkoxy, phenoxy, phenyl, cyclohexyl, benzyl, halogen and the like) if the solvent character of these radicals is not substantially impaired by the substituents. Suitable reactive groups are customary groupings which are known from high-grade finishing and the chemistry of reactive dyestuffs and which contain at least one removable radical which, in the presence of suitable catalysts, and optionally under the action of heat, is able to react with the functional groups of the said types of fibre with the formation of a covalent bond.

A large number of such groupings are described in the literature, for example in "The Chemistry of Synthetic Dyes", Volume VI, Chapter 1, edited by Venkataraman and in British Patent Specification 1,378,244, page 1, line 15 to page 3, line 60 (with the exception of the reactive groups which are capable of undergoing an addition reaction).

Preferred reactive compounds are formaldehyde derivatives of organic nitrogen compounds, especially those of the formula

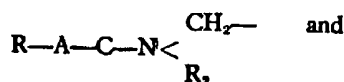


wherein

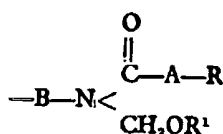
R represents an optionally substituted alkyl, alkenyl, cycloalkyl, aryl or aralkyl radical with 6 to 22 C atoms,

A represents a direct bond or a divalent bridge member,

R¹ represents hydrogen, an optionally substituted alkyl, alkenyl, aryl, aralkyl or acyl radical or the radical



R² represents hydrogen, an optionally substituted alkyl, alkenyl or aralkyl radical, the radical CH₂OR¹ or the radical



in which

B denotes a divalent, optionally substituted aliphatic, araliphatic, aromatic-carbocyclic or cycloaliphatic radical

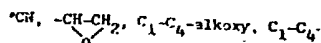
with the proviso that A is a divalent bridge member if R¹ is hydrogen.

The alkyl radicals R can be interrupted by oxygen atoms and substituted by substituents, for example, C₁—C₁₈-alkoxy, phenoxy, phenyl, cyclohexyl, benzyl, chlorine, bromine or OH.

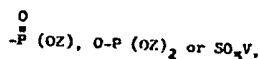
The alkenyl radicals R are preferably unsubstituted. Suitable cycloalkyl radicals are cyclohexyl radicals which can be substituted, for example by C₁—C₄-alkyl, and chlorine.

Suitable aryl and aralkyl radicals R and R¹ are phenyl and phenyl-C₁—C₄-alkyl radicals which can be substituted in the benzene nucleus by C₁—C₄-alkyl, C₁—C₄-alkoxy, chlorine and bromine.

Suitable alkyl radicals R² and R³ are those with 1—6 C atoms which can be interrupted by oxygen bridges and substituted by substituents, for example, OH, Cl, Br,



-alkoxycarbonyl or the radicals



in which

V represents H or a cation and

Z represents V or C₁—C₄-alkyl or hydroxy-C₁—C₄-alkyl.

Suitable alkenyl radicals R₁ and R₂ have 3 to 4 C atoms.

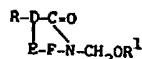
Suitable acyl radicals R¹ are C₁—C₄-alkylcarbonyl, benzoyl or toluyl radicals as well as the radical —CO—CH=CH—COOV. Possible cations are K, Na and ammonium ions.

Suitable radicals A are —O—, —NH—, —N(C₁—C₄-alkyl)— or



Suitable radicals B are C₂—C₁₀-alkylene, phenylene, toluylene, cyclohexylene and C₁—C₄-alkylene-phenylene-C₁—C₄-alkylene.

Further suitable reactive compounds a) correspond to the formula



(II)

wherein

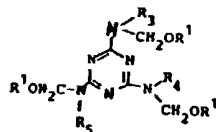
R and R¹ have the abovementioned meaning and

D represents CH or N;

E represents C₁—C₃-alkylene and

F represents a direct bond or CO,

and those of the formula

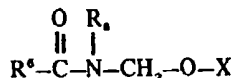


(III)

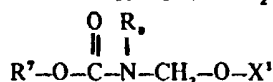
wherein

R¹ has the abovementioned meaning andR₃—R₅ represent CH₂OR¹, R² or R, with the proviso that at least one radicalR₃—R₅ represents R.

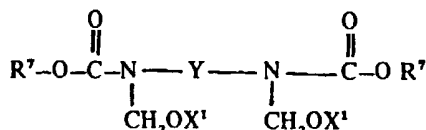
Reactive compounds which are particularly suitable for the process are those of the formulae



IV

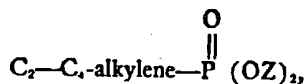
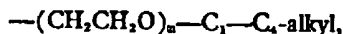


V and



VI

in which

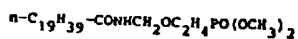
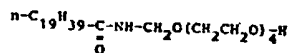
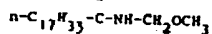
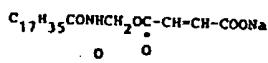
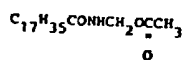
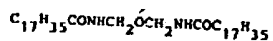
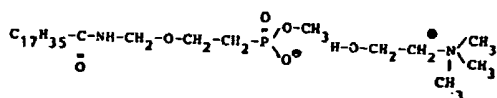
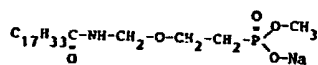
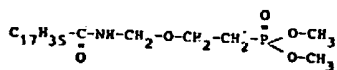
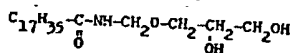
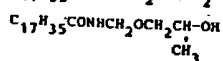
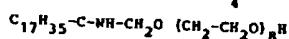
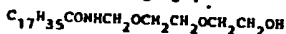
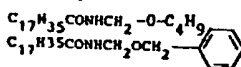
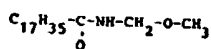
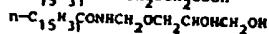
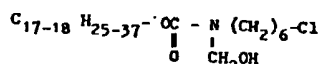
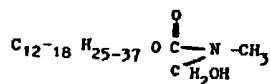
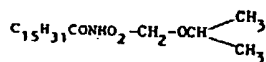
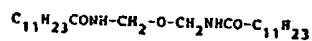
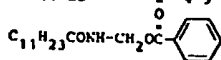
R⁶ represents a C₁₁—C₁₇-alkyl radical or alkenyl radical or represents a phenyl or benzyl radical which is optionally substituted by chlorine or bromine,R⁷ represents a C₁₂—C₁₈-alkyl radical or alkenyl radical.R⁸ represents hydrogen of C₁—C₄-alkyl andX represents C₁—C₆-alkyl, C₃—C₄-alkenyl, benzyl, mono- or poly-hydroxy-C₁—C₆-alkyl, —(CH₂CH₂O)_n—H, —(CH₂CH—O)_n—H,

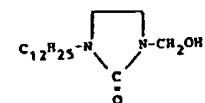
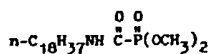
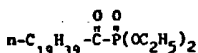
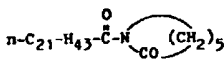
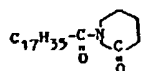
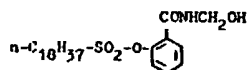
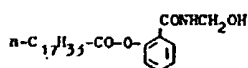
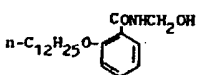
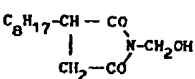
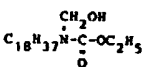
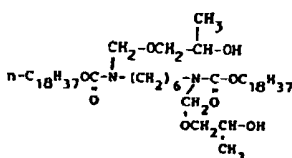
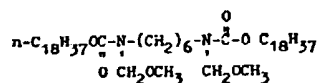
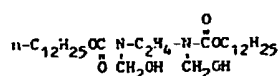
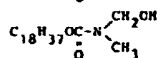
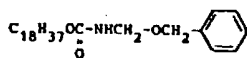
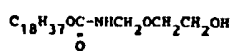
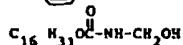
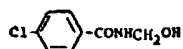
in which

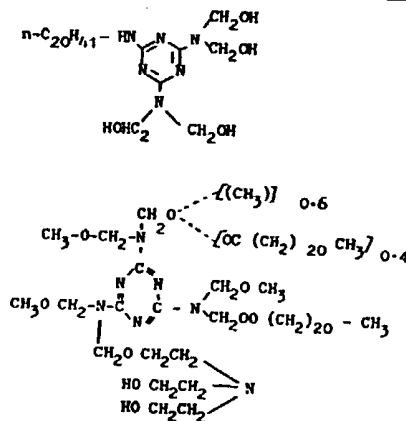
Z and V have the abovementioned meaning

Y represents C₂—C₄-alkylene, phenylene or toluylene andX¹ stands for X or hydrogen.

The following fibre-reactive compounds a) may be mentioned by way of example (particularly preferred being an N-methylol derivative of a long chain fatty acid amide, or an N-methylol derivative of a carbamic and ester of a long chain alcohol): methylol compounds of stearylurea and of laurylurethanes, stearylurethanes, stearylethyleneimine-urea, benzamide, chlorobenzamide, salicylamide and caprolactam, and also compounds of the formulae:







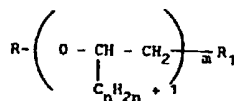
The compounds described above are known in some cases, or they are readily accessible by methods which are in themselves known. The formaldehyde derivatives which are preferably to be used are obtained, for example, by reaction of corresponding compounds containing amino groups (amides, ureas and urethanes) with formaldehyde in the presence of an alkali and, if necessary, subsequent etherification or esterification, which are carried out in a customary manner. Methods of this type are described, for example, in Org. Reactions 14 (1965), pages 52—269, Helv. Chim. Acta 24, (1941), pages 302 et seq., DT—OS (German Published Specification) 2,313,554 and U.S. Patent Specifications 2,361,185 and 2,313,742.

Substances which can be used as catalysts b) are customary substances known from high-grade finishing. Suitable catalysts for the reactive compounds of the formula I which are preferably to be employed are acid donors, such as ammonium chloride and ammonium sulphate or the chlorides, nitrates and perchlorates of magnesium or zinc, as well as aluminium sulphate.

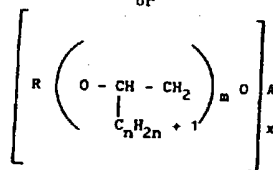
Suitable catalysts for reactive compounds which react with the OH or NH groups of the fibres with elimination of hydrogen halides are customary alkaline compounds, such as alkali metal hydroxides, carbonates and bicarbonates.

Suitable swelling agents to be employed according to the process are, above all, customary cellulose swelling agents which are not volatile under the conditions of transfer printing or thermofixing.

Examples of swelling agents which may be mentioned are: caprolactam, ethylene glycol, diethylene glycol, dipropylene glycol, butanediol, hexanediol, glycerol, sorbitol, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, triethylene glycol, pentaglycol, butanediol, ethylene glycol monoacetates, acetic acid glycerol ester, diethylene glycol monomethyl ether-acetate, polyethylene oxides and polypropylene oxides with molecular weights of 200 to 1,000, oxyethylated nonylphenol and polyethers according to British Patent Specification 1,249,896 (DOS (German Published Specification) 1,811,796) of the general formula



or



wherein

$n=0$ or 1 ,

$m=2$ to 20 ,

$\text{R}=\text{H}$, alkyl, aralkyl, alkaryl, $-\text{COR}_2$, SO_2R_2 or CO_2R_2 ,

R_2 =alkyl, cycloalkyl, aralkyl or aryl,

$R_1 = OH, OR_2, SR_2, NHR_2, OCOR_2, OSO_2R_2$ or $NH\text{-aryl}$,

$x = \text{number of unsaturated valencies in A and}$

$A = ROCH_2CHORCH_2, CH_2\text{---}CHORCH_2\text{---}(CH_2)_x C$ or $CH_2C(CH_2OR)_x$.

The amount to be employed depends on the substrate to be dyed, the nature of the dyestuff and other parameters and for a particular case must be determined by simple preliminary experiments.

Phosphoric acid alkyl esters, such as dibutyl phosphate, are also very suitable as swelling agents.

Suitable crosslinking agents for improving the crease characteristics are reactant resins and melamine resins, but also urea-formaldehyde resins, for example, the following substances: dimethylolurea, dimethylolethyleneurea, dimethylolpropyleneurea, dimethyloldihydroxyethyleneurea, trimethylolmelamine, trimethoxymethylmelamine, hexamethoxymethylmelamine, dimethylolhydroxyethyltriazone, dimethylolmethyl carbamate, dimethylolethyl carbamate, dimethylolhydroxyethyl carbamate, N-methylolacrylamide, glyoxal, tetraoxane, chloral hydrate, glutaraldehyde and epichlorohydrin.

Water-soluble, masked isocyanates, especially bisulphite adducts of customary isocyanates, such as are described, for example, in Liebigs Annalen, Volume 562, page 205 et seq., Angew. Chemie, Volume 49, page 257 et seq. and German Patent Specification 859,156, are also suitable.

Use of the bisulphite adducts in the form of their aqueous or aqueous-organic solutions which are stable on storage and contain 0.5 to 20 per cent by weight (relative to the bisulphite adduct) of an aromatic sulphonic acid (preferably toluenesulphonic acid), in accordance with DT-OS (German Published Specification) 2,414,470, is preferred.

Textile sheets and sheet-like structures such as woven fabrics, knitted fabrics, fleeces, sheets and carpets are suitable for the process according to the invention.

Preferred fibre materials are those made of cellulose fibres, for example, cotton, rayon staple, line jute and hemp, as well as natural polyamides, such as wool, silk and leather.

Synthetic polyamides, and also composite structures of the fibre materials previously mentioned and fibre materials made of cellulose esters, polyurethanes, polyamides, polyacrylonitrile, and, in particular, aromatic polyesters, are also suitable for the process according to the invention.

The reactive substances according to the invention are used in amounts of 1—10%, and preferably in amounts of 2—6%, relative to the textile goods.

The amounts of catalysts to be employed can be 0.5—10%, and preferably 2—5%, relative to the reactive substances.

The amounts of swelling agents employed can vary, depending on the nature of the textile goods. The amounts used are 1—5% relative to the textile goods. However, the process is preferably carried out without the addition of swelling agents. The addition of crosslinking agents for improving the crease characteristics can vary within wide limits, depending on the effect desired. The amount can be 2—14%, and preferably 3—8%, relative to the substrate.

The application of the abovementioned substances according to the invention to the textile goods can be effected from an aqueous liquor or from organic solvents, preferably from perchloroethylene, depending on which method is suitable.

In order to prepare the aqueous liquors, the fibre-reactive compounds, in the case where these do not possess any groups conferring solubility, are preferably employed together with 1—20%, and especially with 5—10% (relative to fibre-reactive compounds) of a customary anionic, cationic, non-ionic and/or amphoteric emulsifier or dispersing agent. In addition, yet further auxiliaries, such as solubilising agents or thickeners, can be added to the liquors.

The aqueous liquors, or the batches of suitable substances according to the invention in perchloroethylene, can be applied to the textile goods by dipping and squeezing off, or can be sprayed on. The batches of the substances according to the invention can also be applied by slop-padding on one side or on both sides. When the process is carried out in practice, the procedure is, for example, that the impregnating liquor is applied to the textile sheet or sheet-like structure by means of a padder. After drying at temperatures of 80 to 120° C, and preferably of 100—110° C—for example in a stenter frame—the textile is ready for the actual dyeing/printing process. In one process variant, the textile sheet or sheet-like structure is brought, for this purpose, into close contact with a so-called temporary support for transfer printing and exposed to a temperature of 160 to 250, and preferably 180 to 220, °C for 15 to 90, and preferably 30 to 60, seconds. During this process, the dyestuff which has been applied to

the temporary support transfers to the substrate, where it is fixed at the same time. The preparation of the temporary supports used with this method is in itself known. Those based on paper are preferably employed.

In the other process variant, the textile, which has been treated with the impregnating liquor described above and dried, is padded or printed in a conventional manner with a dyestuff dispersion, dried again (at 80° to 100° C) and then subjected to a dry heat treatment at 160° to 240° C, and preferably 180° to 220° C, whereupon the dyestuff is fixed and the crosslinking agent is crosslinked at the same time.

The condensation of the formulation to be used according to the invention can, however, be carried out by means of a heat treatment at 130—190° C before employing the actual dyeing or printing method.

This heat treatment can be carried out, for example, at 130° C for 4 minutes, at 180—190° C for 30 seconds or at 150—160° C for 2—3 minutes.

A so-called shock condensation is also possible in the case of lightweight goods. In this, the impregnated textile goods are subjected to the heat treatment at 130—190° C without prior drying. The textile goods can then be printed or dyed by the principle of heat transfer printing or of thermofix dyeing.

The dyed or printed textile can in every case be subjected to an after-treatment with heat, for the complete condensation reaction of the reactive compounds.

Dyestuffs which can be used for dyeing and printing in accordance with the principle of transfer printing are commercially available dyestuffs for transfer printing, preferably sublimable disperse dyestuffs of all categories which are readily soluble in the compound (I), as a result of the radicals R.

Examples which may be mentioned are 1 - amino - 2 - phenoxy - 4 - hydroxy-anthraquinone, 1 - amino - 2 - bromo - 4 - hydroxyanthraquinone, 1 - amino - 2 - cyano - 4 - ethylaminoanthraquinone, 1,4 - diaminoanthraquinone, 4' - nitro - 4 - aminoazobenzene, 2' - cyano - 4' - nitro - 4 - (bis - ethyl) - aminoazobenzene, 3 - hydroxyquinophthalone, and the condensation product of 2 - methyl - 4 - (bis-hydroxyethyl) - aminobenzaldehyde and malodinitrile.

The customary thermosol disperse dyestuffs are suitable for the thermofixing process.

Polyester/cellulose mixed fabrics impregnated according to the invention can be printed particularly advantageously by the thermofixing method.

In general, the textiles which have been impregnated according to the invention and printed display a very pleasing, soft handle of the goods and excellent crease characteristics as well as good fastness properties in use.

With the process according to the invention it is possible to use padding liquors which contain only disperse dyestuffs which dye both the polyester part and the pretreated cellulose part in a solid shade.

On the other hand, the impregnated mixed fabric can be padded or printed with a mixture of disperse dyestuffs and reactive dyestuffs and by this means, after thermofixing, the cellulose fibres are dyed by the reactive dyestuffs and the polyester fibres are dyed by the disperse dyestuff, in the customary manner.

Compared with the processes which are known from German Offenlegungsschriften (German Published Specifications) 1,975,262, 2,045,465, 2,219,978, 2,418,519, 2,436,782 and 2,453,362 for printing cellulose materials in accordance with the principle of transfer printing, the dyeings and prints produced by the process according to the invention display a number of technological advantages, for example, improved fastness to rubbing and/or wet processing, a higher dye yield, an improved handle and no troublesome odours. The textile goods treated according to the invention exhibit particularly pleasing, soft handle characteristics and good crease characteristics.

In the example which follows "parts" denote parts by weight.

Example 1.

A fabric made of polyester/cotton (50:50) is impregnated with a padding liquor consisting of 60 parts of a compound of the formula



10 parts of a compound of the formula $C_{12-18}H_{23-27}OCON(CH_2)_6-Cl$,



30 parts of methylol caprolactam,

60 parts of hexamethylolmelamine hexamethyl ether,

5 parts of an emulsifier on the basis of oleyl alcohol/ethylene oxide, 5 parts of ammonium sulphate and 830 parts of water, squeezed off to a liquor pick-up of about 70%, dried for 3 minutes at 100° C and subsequently heated for 3 minutes at 150° C.

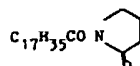
5 The goods prepared in this way are brought into contact with a transfer printing paper, which has been printed with Disperse Red 60 (C.I. 60,756), for 30 seconds at 210° C. 5

A brilliant red print which has good fastness properties in use and in particular comparatively good fastness to wet processing and rubbing, is obtained.

10

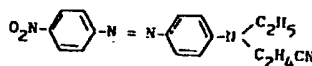
Example 2.

A cotton fabric is impregnated with a padding liquor consisting of 60 parts of the compound of the formula $C_{17}H_{35}CONHCH_2OCH_3$, 10 parts of the compound of the formula 10



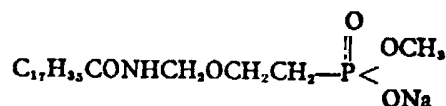
15 80 parts of hexamethylmelamine hexamethyl ether, 5 parts of sodium dodecylbenzene-sulphonate, 5 parts of ammonium sulphate and 840 parts of water, squeezed off to a liquor pick-up of about 90% and dried for 3 minutes at 100° C and subsequently heated for 2 minutes at 160° C. 15

20 The goods prepared in this way are printed as described in Example 1. When the dyestuff used is that of the formula 20



a deep orange print with good fastness properties is obtained. Analogous results are obtained when 15 parts of the compound

25



25

or 35 parts of the compound $C_{17}H_{35}CONHCH_2OC_4H_9$, are employed in place of the reactive component mentioned.

Example 3.

30 A 67:33 polyester/rayon staple fabric is impregnated with a padding liquor consisting of 200 parts of the reactive component described below, 50 parts of hexamethylmelamine hexamethyl ether, 5 parts of ammonium sulphate and 745 parts of water, squeezed off to a liquor pick-up of about 100%, dried at 100° C and subsequently heated for 4 minutes at 150° C. It is then printed in accordance with Example 1. When Disperse Blue 72 (C.I. 60,725) is used as the dyestuff, a blue print with good fastness properties is obtained. 35

The abovementioned reactive component was prepared as follows: 298 g of stearylurea were mixed with 324 g of diethylene glycol monobutyl ether, whilst stirring, and the mixture was heated to 85° C. 160 g of formaldehyde (37% strength) were then added. The mixture was kept at 85° C for 15 minutes and a solution of 40 g of sodium dodecylbenzenesulphonate in 578 g of water was added and the resulting mixture was stirred cold. The pH value of the formaldehyde was adjusted to 8 with sodium carbonate before the addition was made. 40

Example 4.

45 A fabric of polyester/cotton (50:50) is impregnated with a padding liquor containing equal amounts of the reactive component and the emulsifier described in Example 1, 20 parts of a bisulphite adduct of a polyisocyanate, prepared in accordance with DT—OS (German Published Specification) 2,414,470, 50 parts of hexamethylol- 45

melamine hexamethyl ether and 820 parts of water, squeezed off to a liquor pick-up of about 70%, dried at 160° C and subsequently heated for 60 seconds at 180° C.

The fabric treated according to the invention is printed in accordance with Example 1. A brilliant red print with good fastness properties in use and good crease characteristics is obtained.

Equally good results are obtained when 200 parts of a composition consisting of 190 parts of the compound $(C_{11}H_{23}CONH-CH_2)_2O$, 200 parts of diethylene glycol monobutyl ether, 15 parts of sodium dodecylbenzenesulphonate and 595 parts of water are employed in place of the reactive component described in Example 1.

Example 5.

A polyester/wool fabric (55:45) is impregnated with a padding liquor containing equal amounts of the reactive component and the emulsifier in Example 1, 35 parts of a bisulphite adduct of a polyisocyanate, prepared in accordance with DT-OS (German Published Specification) 2,414,470, 5 parts NH_4Cl and 855 parts of water, squeezed off to a liquor pick-up of about 100%, dried at 110° and subsequently heated for 3 minutes at 140° C.

It is then printed in accordance with Example 1. When Disperse Blue 26 (C.I. 63,305) is used as the dyestuff, a turquoise-coloured print with good fastness properties in use is obtained.

Example 6.

A polyester/rayon staple fabric (67:33) was impregnated with a padding liquor consisting of 100 parts of the condensation product of 1 mol of hexamethylmelamine pentamethyl ether, 1.8 mols of behenic acid and 0.9 mol of triethanolamine (in accordance with French Patent Specification 1,065,686), 30 parts of 40% strength acetic acid, 3 parts of aluminium sulphate, 50 parts of diethylene glycol monobutyl ether and 817 parts of water, squeezed off to a liquor pick-up of about 100%, dried at 100° C, subsequently heated for 3 minutes at 150° C and printed in accordance with Example 1. When Disperse Yellow 3 (C.I. 11,855) is used as the dyestuff, a yellow print with good fastness properties is obtained.

Example 7.

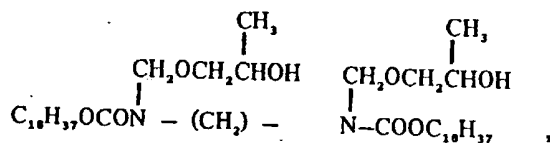
A fabric of 100% cotton was impregnated with a padding liquor consisting of 200 parts of the mixture described below, 30 parts of a bisulphite adduct of a polyisocyanate, prepared in accordance with DT-OS (German Published Specification) 2,414,470 and 770 parts of water, squeezed off to a liquor pick-up of about 90%, dried at 120° C and printed in accordance with Example 1. When 1 - amino - 2 - cyano - 4 - ethylaminoanthraquinone is used, a turquoise-coloured print with adequate fastness properties is obtained.

The above mixture was prepared by mixing:
200 g of the compound $C_{11}H_{23}CONHCH_2OCH_3$,
200 g of diacetic acid glycerol ester.

A solution of 15 g of sodium dodecylbenzenesulphonate in 585 g of water was added to the mixture and the resulting mixture was stirred cold.

In place of the reactive component described, it is also possible, with equal success, to use 200 parts of the composition described below:

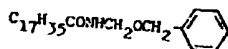
a. 266 parts of the compound



180 parts of diethylene glycol monobutyl ether, 15 parts of sodium dodecylbenzenesulphonate and 539 parts of water,

b. 200 parts of the compound $C_{11}H_{23}CONHCH_2OCOCH_3$, 200 parts of diethylene glycol monobutyl ether, 15 parts of sodium dodecylbenzenesulphonate and 585 parts of water,

c. 250 parts of the compound



150 parts of butane-2,3-diol, 15 parts of sodium dodecyl sulphate and 585 parts of water,

d. 200 parts of N - methylol - benzamide, 200 parts of diethylene glycol monobutyl ether and 600 parts of water, and

e. 200 parts of N-methylol-lauric acid amide, 180 parts of diethylene glycol monobutyl ether, 15 parts of sodium dodecylbenzenesulphonate, 2 parts of sodium polyacrylate and 603 parts of water.

Example 8.

A polyester/cotton fabric (50/50) was impregnated with a padding liquor consisting of 50 parts of stearylethylene-imineurea, 5 parts of sodium dodecylbenzenesulphonate, 40 parts of hexamethylolmelamine hexamethyl ether, ~~50 parts of diethylene glycol butyl ether, 3 parts of ammonium sulphate and 852 parts of water,~~ squeezed off to a liquor pick-up of about 75% and dried at 100° C. The fabric was printed in accordance with Example 1. When a mixture of Disperse Yellow 54 (C.I. 47,020) and Disperse Blue 26 is used as the dyestuff, a clear print with good fastness properties is obtained.

Example 9.

A polyester/cellulose fabric (67:33) was impregnated with a padding liquor consisting of 105 parts of the reactive component described in Example 1, 30 parts of dibutyl phosphate, 10 parts of ammonia (25% strength), 40 parts of hexamethylolmelamine hexamethyl ether and 815 parts of water, squeezed off to a liquor pick-up of about 90% and dried at 100° C. It was then printed in accordance with Example 1. When Disperse Yellow 3 (C.I. 11,855) is used as the dyestuff, a yellow print with good fastness properties is obtained.

Example 10.

A polyester/cotton fabric (50:50) is impregnated with a padding liquor consisting of 200 parts of the reactive component described below, 80 parts of hexamethylolmelamine hexamethyl ether, 5 parts ammonium sulphate and 715 parts of water, dried at 110° C, subsequently heated for 3 minutes at 160° C and then printed as indicated in Example 1.

A clear green print is obtained when a mixture of Disperse Yellow 54 (C.I. 47,020) and Disperse Blue 26 is used as the dyestuff.

The reactive component was prepared as follows:

140 g of stearyl isocyanate were reacted with 106 g of diethylene glycol for 2 hours at a temperature of 90° C, 1 g of tin malcate being added as the catalyst. 62 g of formaldehyde (37% strength), and also 20 g of sodium dodecylbenzenesulphonate, dissolved in 471 g of water, were added. The mixture was stirred for 15 minutes at 85° C. Before the formaldehyde was added, its pH value was adjusted to 8 with sodium carbonate.

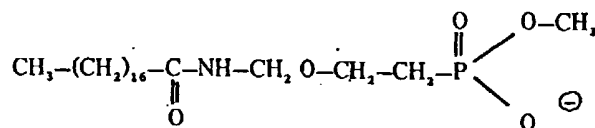
The reaction product was then stirred cold.

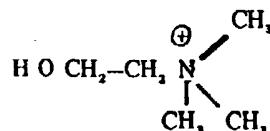
Example 11.

A polyester/cotton fabric (70:50) was impregnated with a padding liquor consisting of 200 parts of the reactive component described below, 40 parts of diethylene glycol monobutyl ether, 40 parts of hexamethylolmelamine hexamethyl ether, 5 parts of ammonium sulphate and 715 parts of water, squeezed off to a liquor pick-up of about 90% and dried for 2 minutes at 160° C. The fabric was then printed in accordance with Example 1.

When Disperse Yellow 3 (C.I. 11,855) is used as the dyestuff, a yellow print with good fastness properties is obtained.

The reactive component mentioned above was prepared as follows: 334 parts of the compound



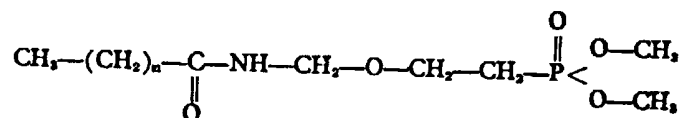


were dissolved in 666 parts of water.

Example 12.

A polyester/cotton fabric (70:30) was impregnated with a padding liquor consisting of 150 parts of the reactive component described below, 40 parts of diethylene glycol monobutyl ether, 50 parts of dimethyloldihydroxyethyleneurea, 5 parts of magnesium chloride and 755 parts of water, squeezed off to a liquor pick-up of about 80% and dried for 3 minutes at 130° C. It was then printed in accordance with Example 1. When Disperse Red 60 (C.I. 60,756) is used as the dyestuff, a red print with good fastness properties in use is obtained.

The reactive component mentioned above was prepared as follows: 300 parts of the compound:



were emulsified with 680 parts of water and 20 parts of a commercially available emulsifier (for example an oxyethylated nonylphenol or sodium alkylbenzenesulphonate).

Example 13.

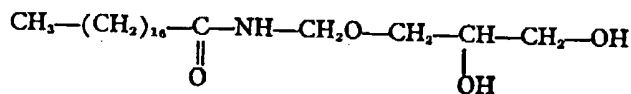
A polyester/cotton fabric (50:50) was impregnated with a padding liquor consisting of 40 parts of the compound $\text{C}_{17}\text{H}_{35}\text{CONH---CH}_2\text{O(CH}_2\text{---CH}_2\text{---O)}_4\text{H}$, 30 parts of diethylene glycol monobutyl ether, 50 parts of dimethylolpropyleneurea, 5 parts of ammonium sulphate and 875 parts of water and squeezed off to a liquor pick-up of about 80%. It was dried for 2 minutes at 120° C and printed in accordance with Example 1.

When Disperse Blue 26 (C.I. 63,305) is used as the dyestuff, a turquoise-coloured print with good fastness properties is obtained.

Example 14.

A polyester/cotton fabric (70:30) was impregnated with a padding liquor consisting of 200 parts of the reactive component described below, 40 parts of hexamethylolmelamine hexamethyl ether, 5 parts of ammonium sulphate and 755 parts of water, squeezed off to a liquor pick-up of 80%, dried for 2 minutes at 130° C and subsequently heated for 2 minutes at 160° C. The fabric was printed in accordance with Example 1. When Disperse Yellow 54 (C.I. 47,020) is used as the dyestuff, a yellow print with good fastness properties is obtained.

The reactive component mentioned was prepared by mixing the following substances: 253 parts of the compound of the formula

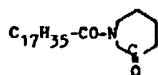


67 parts of diethylene glycol monobutyl ether, 20 parts of sodium dodecylbenzenesulphonate and 660 parts of water.

Example 15.

A polyester/cotton fabric (50:50) was impregnated with a padding liquor consisting of 200 parts of the reactive component described below, 50 parts of hexamethylolmelamine hexamethyl ether, 5 parts of ammonium sulphate and 745 parts of water and squeezed off to a liquor pick-up of about 75%. It was dried for 4 minutes at 160° C and printed in accordance with Example 1. When Disperse Blue 72 (C.I. 60,725) is used as the dyestuff, a blue print with good general fastness properties is obtained.

The reactive component was prepared by mixing the following substances: 217 parts of stearic acid amide-methylolmethyl ether, 35 parts of the compound



200 parts of dipropylene glycol, 24 parts of sodium dodecylbenzenesulphonate and 524 parts of water.

Example 16.

A cotton fabric was impregnated with a padding liquor consisting of 200 parts of the reactive component described below, 40 parts of triethylene glycol, 5 parts of ammonium chloride and 755 parts of water and squeezed off to a liquor pick-up of about 100%. It was dried for 2 minutes at 120° C and printed in accordance with Example 1. When Disperse Red 60 (C.I. 60,756) is used as the dyestuff, a red print with good fastness properties is obtained.

The reactive component was prepared by mixing the following substances: 190 parts of stearic acid methylolamide, 150 parts of methylol-caprolactam, 20 parts of sodium dodecylbenzenesulphonate and 640 parts of water.

Example 17.

A fabric of polyester/cotton (50:50) was impregnated with a padding liquor consisting of 90 parts of the compound of the formula



20 parts of methylol-caprolactam, 80 parts of hexamethylolmelamine hexamethyl ether, 5 parts aluminium sulphate, 5 parts of a sulphated phenyl-polyglycol ether and 850 parts of water and squeezed off to a liquor pick-up of about 70%. It was dried for 3 minutes at 150° C and printed in accordance with Example 1.

When Disperse Blue 26 (C.I. 63,305) is used as the dyestuff, a turquoise-coloured print with good fastness properties is obtained.

Example 18.

A fabric of polyester/cotton (50:50) is impregnated with a padding liquor consisting of 200 parts of the reactive component described in Example 1, 30 parts of methylolcaprolactam, 60 parts of hexamethylolmelamine hexamethyl ether, 5 parts of aluminium sulphate and 705 parts of water, squeezed off to a liquor pick-up of about 70% and dried for 3 minutes at 130° C. It is subsequently heated for 3 minutes at 150° C.

The goods prepared in this way are brought into contact with a transfer printing paper, which has been printed with Disperse Red 60 (C.I. 60,756), for 30 seconds at 220° C.

Example 19.

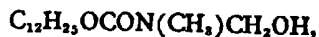
A fabric of polyester/cotton (50:50) is impregnated with a padding liquor consisting of 100 parts of the reactive component prepared in accordance with DT—OS (German Published Specification) 2,414,470 described in Example 1, 80 parts of squeezed off to a liquor pick-up of about 70%, dried at 140° C.

The fabric treated according to the invention is printed in accordance with Example 1. A brilliant red print which has good fastness properties in use and good crease characteristics is obtained.

Example 20.

A polyester/cotton fabric (50:50) was impregnated with a padding liquor consisting of 80 parts of a compound of the formula $\text{C}_{12}\text{H}_{25}\text{OCON}(\text{CH}_2)_2\text{CH}_2\text{OH}$ 20 parts of methylolcaprolactam, 80 parts of a hexamethylolmelamine methyl ether, 5 parts of an emulsifier based on oleyl alcohol and ethylene oxide, 5 parts of aluminium sulphate and 810 parts of water, and squeezed off to a liquor pick-up of 70%. It was dried at 120° C, subsequently heated for 3 minutes at 150° C and printed in accordance with Example 1.

If Disperse Blue 72 (C.I. 60,725) is used as the dyestuff, a blue print with good fastness properties is obtained. 80 parts of a compound of the formula



30 parts of hexamethylmelamine hexamethyl ether, 5 parts of an emulsifier based on oleyl alcohol and ethylene oxide, 5 parts ammonium sulphate and 780 parts of water, squeezed of to a liquor.

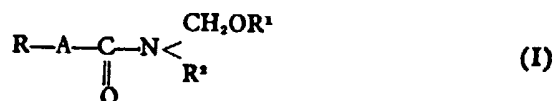
5 WHAT WE CLAIM IS:—

1. A process for dyeing or printing a textile sheet or sheet-like structure which consist wholly or partly of fibres containing OH or NH groups with a disperse dye-stuff by the principle of heat transfer printing or by the thermofixing method, in which the sheet or sheet-like structure is impregnated with a liquor containing (a) 10 a reactive compound (as hereinbefore defined) and (b) a compound which catalyses this condensation reaction selected from aluminium chloride, aluminium sulphate, ammonium sulphate and zinc or magnesium chloride, nitrate and perchlorate, is dried and is dyed by the thermofixing dyeing method or is transfer printed after fixing the said reactive compound.

15 2. A process according to claim 1, in which the liquor further contains a fibre-swelling agent.

3. A process according to claim 1 or 2, in which the liquor further contains a cross-linking agent.

20 4. A process according to any of the foregoing claims, in which the reactive compound (a) is of the general formula

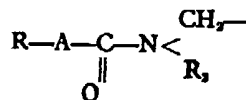


in which

R denotes an optionally substituted alkyl, alkenyl, cycloalkyl, aryl or aralkyl radical with 6 to 22 carbon atoms,

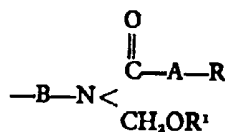
25 A denotes a direct bond or a divalent bridge member,

R¹ denotes a hydrogen atom, an optionally substituted alkyl, alkenyl, aryl, aralkyl or acyl radical or a radical of the general formula



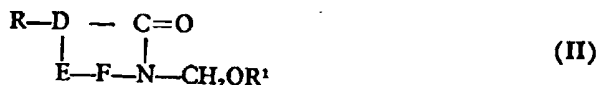
and

30 R² denotes a hydrogen atom, an optionally substituted alkyl, alkenyl or aralkyl radical, a radical CR₂OR¹ or a radical of the general formula



in which B denotes a divalent, optionally substituted aliphatic, araliphatic, aromatic-carbocyclic or cyclo-aliphatic radical, and R and R₁ have the above-mentioned meanings, with the proviso that A is a divalent bridge member if R¹ is hydrogen.

35 5. A process according to any of claims 1 to 3, in which the reactive compound (a) is of the general formula



in which

40 R and R¹ have the same meanings as in claim 4 and D denotes CH or N;

E denotes a C₁ to C₃ alkylene radical and

F denotes a direct bond or CO.

6. A process according to any of claims 1 to 3, in which the reactive compound (a) is of the general formula

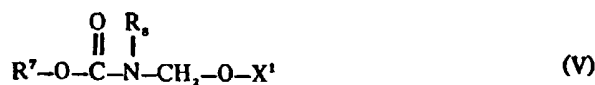


in which

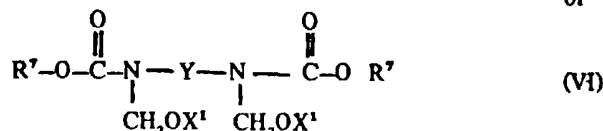
R¹ has the same meaning as in claim 4 and

R₅, R₄ and R₃ independently have the same meanings as R₂ or R₁ in claim 4 or denote —CH₂OR¹, with the proviso that at least one radical R₅, R₄ and R₃ has the same meaning as R.

7. A process according to any of claims 1 to 3, in which the reactive compound (a) is of the general formula



or



in which

R⁶ denotes a C₁₁ to C₁₇ alkyl or alkenyl radical or denotes a phenyl or benzyl radical which is optionally substituted by chlorine or bromine,

R⁷ denotes a C₁₂ to C₁₈ alkyl or alkenyl radical,

R⁸ denotes a hydrogen atom or a C₁ to C₄ alkyl radical

and

X denotes a C₁ to C₆ alkyl, C₂ or C₄ alkenyl, benzyl, mono- or poly-hydroxy-

C₁ to C₆ alkyl, —(CH₂CH₂O)_n—H, —(CH₂CH—O)_n—H,

CH₃

—(CH₂CH₂O)_n—C₁ to C₆ alkyl

$\begin{array}{c} \text{O} \\ || \\ \text{R}^6\text{---C---NH---CH}_2\text{---} \end{array}$, —CH₂COOZ, C₂—C₆-alkylene-SO₂V or

$\begin{array}{c} \text{O} \\ || \\ \text{C}_2\text{---C}_6\text{-alkylene---P(OZ)}_2 \end{array}$ radical,

in which

V denotes a hydrogen atom or a cation,

Z denotes a C₁ to C₆ alkyl or hydroxy-C₁ to C₆ alkyl radical or has the same meaning as V, and

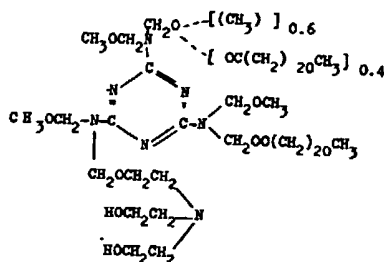
Y denotes a C₂ to C₆ alkylene, phenylene or toluylene radical

X₁ denotes X or H.

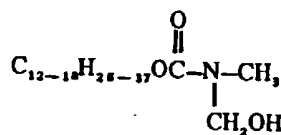
8. A process according to any of claims 1 to 3, in which the reactive compound (a) is an N-methylol derivative of a long chain fatty acid amide, or an N-methylol

9. A process according to any of claims 1 or 3, in which the reactive compound

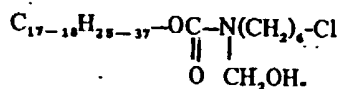
(a) is the compound of the formula



10. A process according to any of claims 1 to 3, in which the reactive compound (a) is any of those hereinbefore specifically identified, other than the compound of claim 9, methylol compounds of laurylurethanes or of caprolactam and compounds of the formula



and



11. A process according to claim 2, or any of claims 3 to 10 as dependent on claim 2, in which the organic swelling agent is a cellulose swelling agent which is not volatile under the dyeing conditions.

12. A process according to any of the foregoing claims, in which the liquor contains a bisulphite adduct of an isocyanate or synthetic resin precondensate as an agent for improving the crease characteristics of the textile sheet or sheet-like structure.

13. A process according to any of the foregoing claims, in which the disperse dyestuff is any of those hereinbefore specifically mentioned.

14. A process according to any of the foregoing claims, in which the impregnated sheet or sheet-like structure is pre-dried at 80 to 100° C.

15. A process according to any of the foregoing claims, in which the pre-dried impregnated sheet or sheet-like structure is brought into close contact with a dyed or printed temporary support for transfer printing and heated to temperatures of 160 to 250° C for 30 to 60 seconds.

16. A process according to claim 15, in which the heating is 180 to 220° C.
17. A process according to any of the foregoing, in which the heating is 180 to 220° C.

17. A process according to any of the foregoing claims, in which the sheet or
sheer-like structure is of cellulose mixed with polyester fibres.

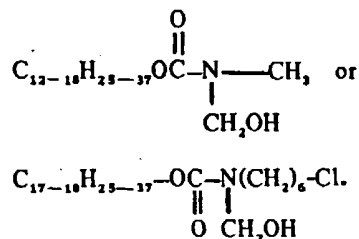
18. A process according to any of the foregoing claims, in which the pre-dried impregnated sheet or sheet-like structure is subjected to a heat treatment at 130—190°C and is subsequently printed by the transfer printing process.

19. A process according to any of claims 1 to 17, in which, following the impregnation with the liquor, the sheet or sheet-like structure is dried and is dyed or printed whilst, at the same time, fixing the reactive compound.

20. A process according to claim 1, when carried out substantially as described in any one of Examples 8, 12, 13 and 16.

21. A process according to any of claims 1 to 17, in which, following the impregnation with the liquor, the sheet or sheet-like structure is dried at 100 to 120° C, subjected to a heat treatment at 130 to 190° C to fix the reactive compound and dyed or printed.

22. A process according to claim 21, in which the reactive compound is a methylol caprolactam or a compound of the formula



23. A process according to claim 1 when carried out substantially as described in any one of the Examples 5, 10 and 15.

24. A textile sheet or sheet-like structure when dyed and/or printed by the process of any of claims 21 to 23.

25. A textile sheet or sheet-like structure when dyed and/or printed by the process of claim 19 or 20.

26. A process according to any of claims 1 to 3, and any of claims 11 to 17 as dependent on claims 1 to 3, in which the reactive compound (a) is a methylol compound of a laurylurethane.

27. A process according to claim 1, when carried out substantially as described in any one of Examples 1 to 4, 6, 7, 9, 11, 12, 14 and 17 to 20.

28. A textile sheet or sheet-like structure, when dyed and/or printed by the process of any of claims 1 to 18, 26 and 27.

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 (72) Inventor ROBERH KUTH



(54) TRANSFER PRINTING PROCESS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for printing sheets or sheet-like structures of synthetic or partially synthetic polymeric materials in accordance with the principle of transfer printing, which process is characterised in that a dyestuff of the formula

Patent Specification 1,190,889). Paper is preferred.

The printing inks can be printed by customary printing processes (letterpress printing, planographic printing, gravure printing or screen/film printing).

Depending on the printing process, binders which can be used are products which dry by chemical and/or physical means, such as those normally used in textile printing or paper printing.

Thickeners which can be used are, above all, those products which even in low concentration produce a distinct increase in the

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35 The transfer printing process is also generally known (compare, for example, Colour Index, 3rd edition, Volume 2, page 2,480) and, for example, is described in detail in French Patent Specifications 1,223,330, 1,334,829 and 1,585,119).

40 Temporary supports which can be used are sheets or sheet-like structures, such as paper, "Cellophane" (Trade Mark), cotton fabric, linen fabric, and metal foils (compare British

ERRATUM

SPECIFICATION No. 1,554,524

Page 1, Heading (72), Inventor, for ROBERH KUTH read ROBERT KUTH

THE PATENT OFFICE
25th February, 1980

cellulose fibres (for example according to DT-OS (German Published Specification) 2,417,774) and cellulose materials impregnated with crosslinking agents and pre-dried (for example according to DOS (German Published Specification 2,502,590) are suitable.

Prints which have good fastness properties in use are obtained on these substrates by the process claimed.